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^{13}C NMR AND X-RAY CRYSTALLOGRAPHIC
DETERMINATION OF THE STRUCTURES OF
SOME ISOMERIC PHENYLQUINOXALINES

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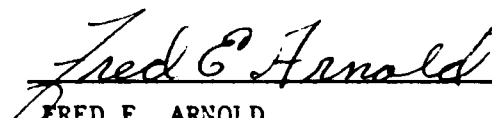
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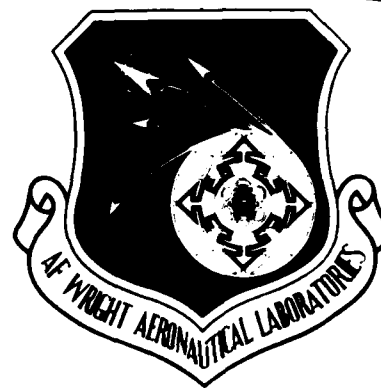
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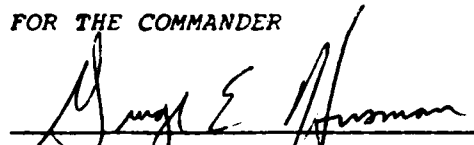
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Unequivocal structural assignments were made for the two isomeric quinoxalines isolated from the reaction of 3-bromobenzil with 4-iodo-o-phenylenediamine as well as for their respective acetylene terminated derivatives. The higher melting isomers were assigned the structures 3-(3-bromophenyl)-2-phenyl-6-iodoquinoxaline and 3-(3-ethynylphenyl)-2-phenyl-6-ethynylquinoxaline, and the lower melting isomers were assigned the structures 2-(3-bromophenyl)-3-phenyl-6-iodoquinoxaline and 2-(3-ethynylphenyl)-3-phenyl-6-ethynyl-quinoxaline. Both x-ray crystallographic analysis and ^{13}C NMR analyses were used and were in complete agreement. For the ^{13}C NMR study, isotropically enriched versions of the quinoxaline isomers were prepared starting from 3-bromobenzil-α'-carboxy-^{13}C. Utilizing substituent effects, all of the ^{13}C absorptions in the molecules were assignable.

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DETERMINATION OF THE STRUCTURES OF SOME ISOMERIC PHENYLQUINOXALINES

12. Continued

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18. Continued

2-(3-Bromophenyl)-3-phenyl-6-iodoquinoxaline
acetylene terminated quinoxalines

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic
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of Dayton Research Institute; and Dr. Michael Barfield, Dr. Steven
R. Walter, Dr. Daniel Draney and Dr. Carl S. Marvel, University of
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INTRODUCTION

The good thermal and hydrolytic stability of polyphenylquinox-
alines has prompted many investigations for characterization and
property correlations for these polymers (References 1-3). The
presence of isomers in polyphenylquinoxalines as a result of the
ring forming polymerization reaction has been noted (Reference 4).
The existence of isomers contributes to the amorphous form of these
polymers and inhibits crystalline polymer formation (Reference 4).
^{13}C NMR spectroscopy has been shown to be useful in establishing
the presence and concentration of different isomeric forms (Refer-
ences 5 and 6). However, the lack of assignments for some carbons
in phenylquinoxaline structures such as
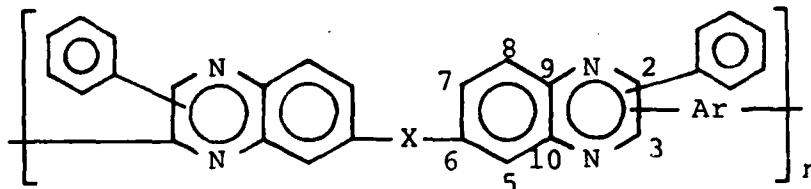
formed from the reaction of aromatic tetraamines with aromatic
tetracarbonyls
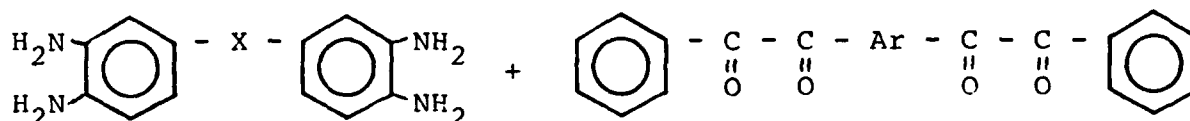
has limited the identification of isomeric forms. The C2 and C3
chemical shifts as well as the chemical shifts of the phenyl car-
bons bonded to the quinoxaline are different in the isomers.
Although Urman et al. (Reference 5) were able to infer a partial
assignment to either C2 or C3 of isomers from the splitting of ^{13}C
peaks caused by different orientation of subsequent repeat units,
the polymers investigated by Relles et al. (Reference 6) did not
reveal this splitting, and chemical shifts were without explana-
tion assigned to C2 and C3. Model compounds were used in both
investigations, but there was uncertainty of the assignments for

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C2 and C3 as well as the directly bonded phenyl carbons in the model compounds. In a report on the ^{13}C NMR of some 5-substituted quinoxaline compounds (Reference 7), the chemical shifts for C2 and C3 were arbitrarily assigned and showed small or no shifts with different substituents.

As part of a development of melt processable resin systems in which an ethynyl group is used to provide a cure mechanism (References 8 and 9), several ethynyl substituted phenyl quinoxaline compounds and oligomers were prepared. The intermediate for one of these ethynyl substituted phenyl quinoxalines (Reference 9) was prepared by reacting 1-(3-bromophenyl)-2-phenylglyoxal with 1,2-diamino-4-iodobenzene to afford a mixture of 2-(3-bromophenyl)-3-phenyl-6-iodoquinoxaline (I) and 3-(3-bromophenyl)-2-phenyl-6-iodoquinoxaline (II). Subsequently, a method was developed to
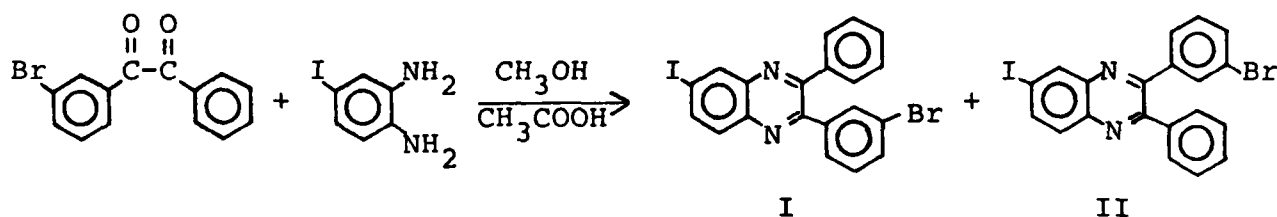
separate isomers I and II (Reference 10), affording a first and unique opportunity to examine the properties of individual quinoxaline isomers. The individual isomers were found to have significant differences in their physical properties. One isomer displayed a lower melting point (95°C versus 182°C), a higher R_f value upon TLC analysis, and a greater solubility in alcoholic solvents than the other isomer (Reference 10). Each isomer was chemically converted to the corresponding acetylene terminated isomers, III and IV. The melting, TLC, and solubility behavior of each acetylene terminated isomer was found to be analogous to its halogenated precursor, i.e. the lower melting halogenated quinoxaline isomer afforded the lower melting acetylene terminated quinoxaline isomer.

HC ≡ C. ... N ... C ≡ CH

III

HC ≡ C. ... N ... C ≡ CH
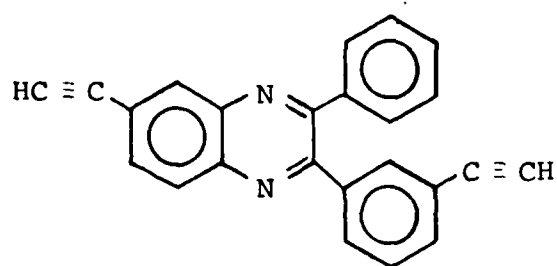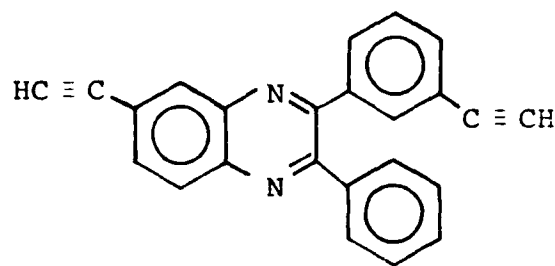
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An initial attempt to assign structures to the low and high melting quinoxaline isomers was made by a study of the ^{13}C NMR spectra of these compounds and an assignment of the ^{13}C chemical shift values for C2 and C3 from a comparison with substituent effects in naphthalenes together with an assumption of additivity of substituent effects (Reference 11). This proved to be useful, but to provide confirmation, additional measurements were made. An x-ray crystallographic analysis of the high melting halogenated quinoxaline isomer afforded an unambiguous assignment of structure II to this compound. This assignment, in turn, permitted further assignment of structure IV to the high melting acetylene terminated derivative of compound II, and structures I and III to the low melting halogenated quinoxaline isomer and its acetylene terminated derivative. Further verification of these structural assignments was obtained through the preparation of ^{13}C enriched versions of compounds I and II starting from 3-bromobenzil-α'-<u>carboxy</u>-^{13}C. An unambiguous assignment was achievable for all of the quinoxaline ^{13}C absorptions as well as the phenyl carbons bonded to the quinoxaline ring. The substituent effect of the quinoxaline ring on phenyl absorptions together with known phenyl substituent effects of the other substituents permits an assignment of all of the ^{13}C absorptions in the low and high melting halogenated quinoxaline isomers as well as in the corresponding low and high melting acetylene terminated quinoxaline isomers. The isomer structure assignments were in complete agreement with those described above from the x-ray crystallographic analysis.

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SECTION II
EXPERIMENTAL

A. SYNTHESIS OF ^{13}C ENRICHED COMPOUNDS

   1. <u>3-Bromobenzil-α'-carboxy-^{13}C</u>

   3-Bromobenzil-α'-<u>carboxy</u>-^{13}C was prepared starting from benzoic acid-<u>carboxy</u>-^{13}C and 3-bromobenzyltriphenylphosphonium bromide by a reported procedure (Reference 12).

   2. <u>2-(3-Bromophenyl)-3-phenyl-6-iodoquinoxaline-3-^{13}C and 3-(3-Bromophenyl)-2-phenyl-6-iodoquinoxaline-2-^{13}C</u>

   2-(3-Bromophenyl)-3-phenyl-6-iodoquinoxaline-3-^{13}C (I) and 3-(3-Bromophenyl)-2-phenyl-6-iodoquinoxaline-2-^{13}C (II) were prepared by the reaction of 3-bromobenzil-α'-<u>carboxy</u>-^{13}C with 4-iodo-<u>O</u>-phenylenediamine in accordance with a reported procedure (Reference 10). Isomer II was isolated and purified by the reported (Reference 10) method. The sample enriched in isomer I used for the ^{13}C NMR study was recovered from the mother liquor obtained from the isolation of isomer II.

B. X-RAY CRYSTALLOGRAPHIC ANALYSIS

   1. <u>Materials</u>

   Single crystals of 3-(3-bromophenyl)-2-phenyl-6-iodo-quinoxaline (isomer IIa in Abstract) are polymorphic, exhibiting a monoclinic and an orthorhombic modification. Both modifications comprise the high melting, low R_f isomer. Crystals of the monoclinic form were grown by vacuum sublimation at 150°C. Ortho-rhombic crystals were prepared by vapor diffusion from an ethanol/isopropanol mixture. Both forms grew as colorless needles.

   2. <u>Methods</u>

   The monoclinic polymorph was subjected to a complete x-ray crystallographic analysis. Unit cell dimensions and space group have been determined for the orthorhombic form. The pertinent crystal data are summarized in Table 1.

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TABLE 1

CRYSTAL DATA FOR MONOCLINIC FORM*

$\underline{a}$ = 9.126(3)Å [18.622(23)] $C_{20}H_{12}N_2BrI$ [$C_{20}H_{12}N_2BrI$]

$\underline{b}$ = 19.521(4) [26.743(24)]   M.W.   487.14 g/mole [487.14]

$\underline{c}$ = 12.199(3) [7.113(10)]   Space Group $P2_{1/c}$ [P_{nma}]

β = 125.59(2)° [90.000]   Z   4 [8]

V = 1767.3Å^3 [3542.3]   F(000)   936 [1872]

D_{meas} = 1.78 g/cc μ(Cu K$_\alpha$)   170.8 cm^{-1} [170.8]

D_{calc} = 1.83 g/cc [1.827] μ(Mo K$_\alpha$)   40.3 cm^{-1} [40.3]

*Corresponding values for the orthorhombic polymorph are given in brackets.

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Unit cell dimensions were determined by least-squares refinement of the angular settings of 12 ($45° < 2\theta < 48°$) reflections. X-ray intensities were measured by using the 2θ step scan technique on a Picker FACS-1 diffractometer employing Nb-filtered Mo K_α (0.71069Å) radiation. Five steps were taken across each peak of width 1.0°. Peak and background count times were 10 seconds. For data in the range $45° < 2\theta < 55°$, the background count times were increased to 20 seconds. Three standard reflections were measured periodically, and no significant change in their intensities was noted. A total of 4,305 intensities were recorded ($2\theta_{max} = 55°$), yielding 4,047 independent reflections. Absorption corrections were not applied.

The structure was solved by the direct phasing method, employing the NORMSF, SINGEN and PHASE subprograms of the XRAY 72 system (Reference 13). The initial E-map revealed peaks which were identified with all nonhydrogen atoms. Hydrogen atoms were located in subsequent difference syntheses.

Atomic coordinates and anisotropic thermal parameters (isotropic for hydrogen) were refined by full-matrix least-squares, using unit weights. Atomic scattering factors for C, N, BR, and I were taken from Cromer and Mann (Reference 14), and those for hydrogen atoms were from Stewart, Davidson and Simpson (Reference 15). The final R value was 0.090. The average shift/error ratio was 0.10. The final atomic parameters are presented in Table 2.

C. ^{13}C NMR ANALYSIS

^{13}C NMR spectra of the ^{13}C enriched samples were recorded on a Bruker Instruments Fourier transform NMR spectrometer operating at a frequency of 62.9 MHz. Samples were analyzed as solutions in chloroform-d as both solvent and internal standard.

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TABLE 2

ATOM COORDINATES AND THERMAL PARAMETERS

(Thermal parameters are in the form $\exp[-2\pi^2(u_{11}h^2a^{*2} + \ldots 2u_{12}hka^*b^* + \ldots)]$.)

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
I	.31363	-.01870	-.34981	.090565	.070937	.065798	.007700	.054572	-.009449
BR	.70904	.41477	.13988	.119454	.054042	.103855	-.029837	.080603	-.011105
C1	.29042	.01774	-.19760	.054433	.045055	.046196	-.066959	.033838	-.001908
C2	.38762	.07266	-.12277	.059853	.043641	.052595	-.008747	.041025	-.007563
C3	.36224	.09774	-.02615	.046104	.034058	.051299	-.003764	.031923	-.005651
C4	.23819	.06506	-.01075	.047523	.036581	.050133	.000267	.029650	-.002031
C5	.14535	.00518	-.08511	.055599	.033466	.068145	-.008276	.041947	-.010833
C6	.17142	-.01821	-.17935	.052983	.044665	.058437	-.008991	.033153	-.012406
N1	.45715	.15330	.04805	.051009	.038787	.052370	-.003037	.037967	-.001866
N2	.20034	.09141	.07520	.046455	.040752	.050831	-.001593	.033954	-.001143
C7	.42405	.17770	.13384	.037491	.035787	.051467	.001590	.028771	-.001801
C8	.28581	.14749	.14047	.039334	.043828	.041693	.000550	.024593	-.003930
C9	.53375	.23661	.21531	.037646	.041591	.044371	-.004740	.025686	-.000170
C10	.56254	.28886	.15133	.049217	.047636	.045489	-.001148	.030463	-.000658
C11	.56994	.34369	.22701	.055354	.046283	.055978	-.012702	.036432	-.013964
C15	.22482	.17841	.22056	.041690	.054057	.048609	-.004157	.030356	-.008793
C16	.17549	.24800	.20455	.046489	.057128	.049884	.006459	.023344	-.006325
C14	.61737	.24048	.35228	.043570	.059086	.043638	.002468	.028160	-.001548
C12	.75488	.34731	.36601	.057592	.051126	.071435	-.012579	.041057	-.025994
C13	.72859	.29480	.42939	.046694	.064204	.055797	-.003309	.029119	-.009669
C17	.09476	.27357	.26325	.064372	.065259	.081489	-.002897	.044085	-.031628
C20	.19879	.13706	.29982	.073856	.059095	.061972	-.011189	.046044	-.008266
C19	.12297	.16557	.36225	.074474	.110989	.067483	-.040004	.056642	-.031123
C18	.06853	.23238	.34231	.059638	.100685	.071431	-.018900	.041928	-.044671
H2	.47463	.09560	-.13300	.0483					
H6	.06728	-.06568	-.25406	.0545					
H10	.51367	.28379	.05660	.0135					
H12	.86010	.38268	.42069	.0581					
H16	.15967	.27289	.12374	.0908					
H17	.04355	.32252	.24460	.0831					
H20	.22565	.09142	.30577	.0426					
H5	.04571	-.01354	-.08490	.0401					
H14	.59447	.21191	.38076	.0533					
H19	.08095	.13785	.40304	.1060					
H18	.0000	.2367	.4250	.060					
H13	.7467	.2900	.5000	.060					

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SECTION III

RESULTS AND DISCUSSION

A. X-RAY CRYSTALLOGRAPHIC DATA

Figure 1 shows a perspective view of the high melting, low R_f halogenated quinoxaline isomer. Selected bond distances and angles are presented in Tables 3 and 4.

B. ^{13}C NMR DATA

The ^{13}C chemical shifts for quinoxaline (References 6, 7, 16, and 17) show that solvent effects cause small differences in reported chemical shifts. The ^{13}C chemical shifts for 2,3-diphenyl quinoxaline have been measured by us (Reference 11) and also reported in the literature (References 5 and 6). These values are shown in Table 5. There appear to be solvent effects on the chemical shifts. There is also a reversal of the chemical shift assignments for the phenyl ortho and meta carbons in our measurements as compared to those of Relles et al. (Reference 6).

The assignment for ^{13}C enriched I and II is shown in Table 6. The numbers assigned to the various carbons are shown in this table. In I the enriched carbon is labeled 3, in II the enriched carbon is labeled 2. Substituent effects and values of coupling constants with the enriched carbons were used to assign chemical shifts.

The substituent effect of the iodo group (-34 ppm) on the directly bonded carbon allows the assignment of C_6. As shown in Table 6, for isomer I ^4Jcc = <0.2 Hz, for isomer II ^5Jcc = 1.59 Hz.

The substituent effect of iodo on the adjacent carbons (+9 ppm) permits the absorptions for hydrogen bearing carbons around 138 ppm to be assigned to either C5 or C7. The large vicinal coupling constant ^3Jcc (6.87 Hz in I and 6.74 Hz in II) with the enriched carbon distinguishes the assignment of C5 from C7. As discussed by Hansen et al. (Reference 18), three bond couplings depend on the dihedral angle in aliphatic compounds (References 19 and 20),
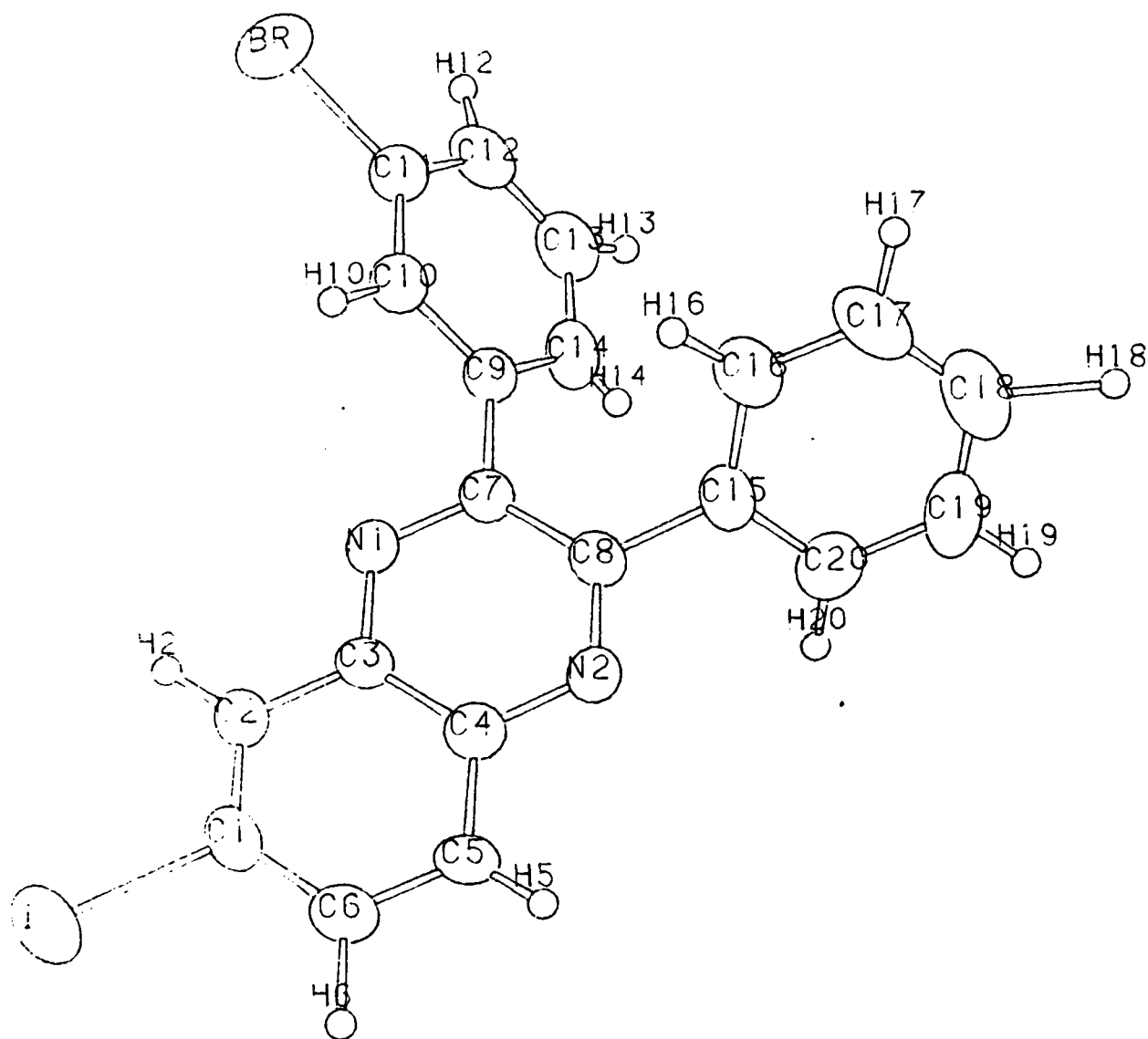
Figure 1. Perspective view of 3-(3-bromophenyl)-2-phenyl-
6-iodoquinoxaline.

TABLE 3

SELECTED BOND DISTANCES

I-C(1)	2.111
Br-C(11)	1.904
N(1)-C(3)	1.354
N(1)-C(7)	1.335
N(2)-C(4)	1.380
N(2)-C(8)	1.311
C(1)-C(2)	1.352
C(1)-C(6)	1.415
C(2)-C(3)	1.414
C(3)-C(4)	1.404
C(4)-C(5)	1.419
C(5)-C(6)	1.380
C(7)-C(8)	1.437
C(7)-C(9)	1.468
C(8)-C(15)	1.504
C(9)-C(10)	1.399
C(9)-C(14)	1.377
C(10)-C(11)	1.380
C(11)-C(12)	1.397
C(12)-C(13)	1.386
C(13)-C(14)	1.389
C(15)-C(16)	1.409
C(15)-C(20)	1.382
C(16)-C(17)	1.385
C(17)-C(18)	1.379
C(18)-C(19)	1.366
C(19)-C(20)	1.408

TABLE 4
SELECTED BOND ANGLES (°)

I-C(1)-C(2)	119.9
I-C(1)-C(6)	116.8
Br-C(11)-C(10)	118.9
Br-C(11)-C(12)	119.3
N(1)-C(3)-C(2)	118.9
N(1)-C(3)-C(4)	121.8
N(1)-C(7)-C(8)	120.3
N(1)-C(7)-C(9)	115.7
N(2)=C(4)-C(3)	120.7
N(2)-C(4)-C(5)	118.2
N(2)-C(8)-C(7)	122.7
N(2)-C(8)-C(15)	114.6
C(1)-C(2)-C(3)	118.4
C(1)-C(6)-C(5)	119.1
C(2)-C(3)-C(4)	119.3
C(3)-C(4)-C(5)	121.1
C(4)-C(5)-C(6)	118.5
C(7)-C(8)-C(15)	122.7
C(7)-C(9)-C(10)	118.0
C(7)-C(9)-C(14)	119.0
C(8)-C(7)-C(9)	124.0
C(8)-C(15)-C(16)	120.4
C(8)-C(15)-C(20)	120.0
C(9)-C(10)-C(11)	118.9
C(9)-C(14)-C(13)	122.3
C(10)-C(9)-C(14)	119.0
C(10)-C(11)-C(12)	121.8
C(11)-C(12)-C(13)	119.1
C(12)-C(13)-C(14)	118.8
C(15)-C(16)-C(17)	119.9
C(15)-C(20)-C(19)	119.1
C(16)-C(15)-C(20)	119.3
C(16)-C(17)-C(18)	120.8
C(17)-C(18)-C(19)	119.2
C(18)-C(19)-C(20)	121.6

TABLE 5

^{13}C CHEMICAL SHIFTS FOR 2,3-DIPHENYLQUINOXALINE
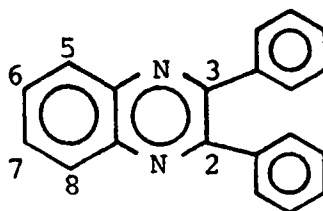
Carbon #	a[6]	b[11]	c[5]
2 = 3	152.5	153.2	154.47
5 = 8	128.4	139.0	
6 = 7	129.7	129.7	
9 = 10	140.2	141.0	

Phenyl Carbons

ortho	127.6	129.6	
meta	129.3	128.1	
para	128.3	128.6	
ipso	138.5	138.9	

TABLE 6

^{13}C CHEMICAL SHIFTS AND Jcc VALUES FOR COMPOUNDS I AND II

I   II
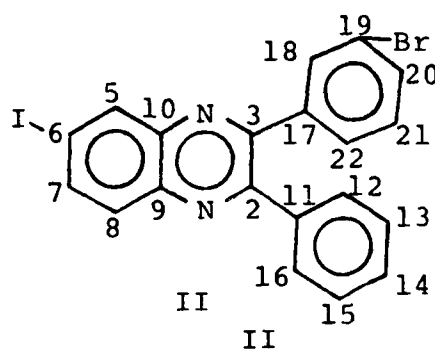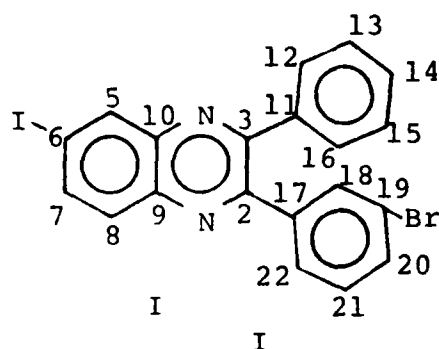
Carbon #	Chemical Shift[c]	Jc,c-3	Chemical Shift	Jc,c-2
2	151.87	52.18	153.56	
3	153.53		152.13	52.1
5	138.04	6.87	138.19	1.64
6	96.01	<0.2	95.64	1.59
7	138.73	1.42	138.98	<0.4
8	130.23	1.52	130.36	6.74
9	140.04	12.97	140.45	4.73
10	141.82	4.73	141.78	12.94
11	138.02	63.48	138.36	63.67
12 = 16	129.65	1.84	129.68	1.80
13 = 15	128.24	4.12	128.31	4.16
14	129.14[b]	1.06	129.15[b]	1.09
17	140.54	6.41	140.64	6.41
18	132.55	1.38	132.76	1.33
19	122.35	<0.2	122.38	<0.2
20	131.86[a]	<0.3	131.98[a]	<0.4
21	129.35[a]	<0.2	129.40[a]	<0.3
22	128.34[b]	0.99	128.45[b]	1.06

[a] The assignments for 20 and 21 may be reversed.

[b] The assignments for 14 and 22 may be reversed.

[c] Chemical shifts in ppm from TMS measured from $CDCl_3$ solvent using 76.91 ppm as the chemical shift of $CDCl_3$.

but are fairly constant in aromatic compounds. The alternative assignment with $^4Jcc = 6.7$ Hz and $^3Jcc = 1.5$ Hz is not likely in view of the results of Hansen et al. (Reference 18) on 1,2,3,4-tetraphenyl naphthalene. They report ^3J C-2,C-8 = 4.08 Hz and ^4J C-2,C-5 = -1.26 Hz.

The assignment for the two directly bonded phenyl carbons C11 and C17 are also made easily from the large ^1Jcc values (63.48 Hz and 63.67 Hz) compared to the ^2Jcc value of 6.41 Hz. The comparable values in 1,2,3,4-tetraphenyl naphthalene are $^1Jcc = 56.31$ Hz and $^2Jcc = 1.80$ Hz (Reference 18).

The assignment for C8 shows that this carbon is shifted downfield from the 2,3-diphenylquinoxaline value. $^4Jcc = 1.52$ Hz in I, $^3Jcc = 6.74$ Hz in II. The assignment for C9 and C10 is dependent on the magnitude of the coupling constants $^3Jcc = 12.97$ in I and 12.94 in II. The ^2Jcc value is smaller, 4.73 Hz in I and II. Comparable values in 1,2,3,4-tetraphenylnaphthalene are 5.97 Hz for ^3Jcc and 0.34 Hz for ^2Jcc (Reference 18).

The assignments for the phenyl carbons are based on known substituent effects for the bromo substituent (Reference 21). In two cases the calculated and observed shifts are sufficiently similar that alternative assignments are possible.

By analogy with I and II and considering substituent effects of an ethynyl group, the chemical shifts for III and IV are shown in Table 7.

In mixtures of the isomers of compounds and oligomers measured by us and in polymers reported in the literature, the C2 and C3 absorptions generally appear as four peaks. Exceptions are a mixture of I and II where there is overlapping of the lowest field absorption, and the polymers reported by Urman et al. (Reference 5) where there is additional splitting of two of the peaks. As reported by Urman et al. (Reference 5) and as can be seen from Tables 6 and 7, the absorptions at lowest and highest field (the outer pair) are due to one isomer and the intermediate absorptions (the inner pair) are due to the other isomer.

TABLE 7

[13]C CHEMICAL SHIFTS FOR COMPOUNDS III AND IV

III   IV
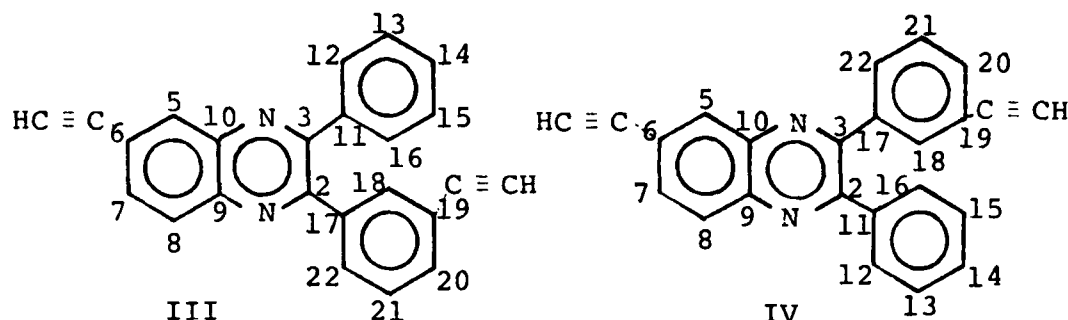
| Carbon #	III Chemical[a] Shift	IV Chemical[a] Shift
2	152.54	153.55
3	153.80	152.90
5	132.75	133.24
6	123.85	123.77
7	132.89	132.92
8	129.00	129.04
9	140.63	140.50
10	140.73	140.95
11	138.13	138.21
12 = 16	129.60	129.64
13 = 15	128.20	128.25
14	129.08	129.14
17	138.90	138.86
18	132.75	132.92
19	122.33	122.38
20	132.38	132.41
21	127.91	127.95
22	130.04	130.08
C≡	82.89,82.67	82.94,82.71
HC≡	77.94,77.66	79.90,77.66

[a]Chemical shifts in ppm from TMS measured from $CDCl_3$ solvent using 76.91 as the chemical shift of $CDCl_3$.

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Although the number of substituents looked at, to date, is small and the substituent effects are small in magnitude, it appears that the chemical shifts of the C2 and C3 carbons can be assigned, using the principle of additivity of substituent effects. This approach has been used by Urman et al. (Reference 5), Relles (Reference 6), and Hedberg et al. (Reference 11).

The operative substituent effects on C2 and C3 of the polymers and compounds described here are that of the substituted phenyl and the substituent on position 6. By comparing the chemical shifts with those in 2,3-diphenylquinoxaline, it can be seen that the substituent effect is relatively large and negative for the carbon to which the substituted phenyl is bonded. Values reported are -0.72 ppm for a para-substituted phenyl by Urman et al. (Reference 5), -1.69 ppm for m-bromo phenyl and -1.07 ppm for m-ethynyl phenyl (Reference 11).

The substituent effect of this substituted phenyl group is, of course, much smaller, in fact almost negligible, on the adjacent C2 or C3. Values reported are -.06 ppm for a para-substituted phenyl (Reference 5), -.18 ppm for m-bromo phenyl and -.09 ppm for m-ethynyl phenyl (Reference 11).

It is proposed that the substituent effect on the C2 and C3 carbons of the substituent on position 6 can be estimated by considering substituent effects in a comparable aromatic system, 2-substituted naphthalenes. Substituent effects in substituted naphthalenes have been frequently studied (Reference 22). Considering the numbering systems used for naphthalenes and quinoxalines,
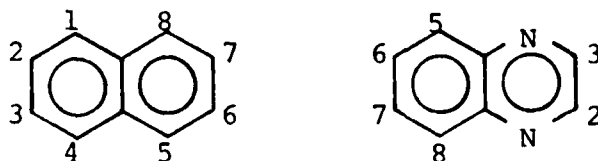
it is proposed that a substituent at the 2 position in naphthalenes will have an effect on carbon 7 similar to the effect that a 6-substituent will have on carbon 3 in quinoxalines. The effect of the 2 substituent on carbon 6 in naphthalenes will likewise be

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similar to the effect of a 6 substituent on carbon 2 in quinoxa-
lines.

In 2-substituted naphthalenes, C7 shows generally a downfield
or positive substituent effect for both electron donating and elec-
tron withdrawing substituents. However, substituent effects at C6
can be positive or negative. They are apparently negative for -OR
substituents, positive for the halogens with the exception of
fluorine and positive for substituents that show resonance effects.

Assuming similar effects in 6 substituted quinoxalines, at least
in sign and relative magnitude, would require that for the halogens in
the 6 position, substituent effects are positive at both C2 and C3 and
of larger magnitude at C3 than C2. The ordering of the four C2 and C3
chemical shifts from lowest to highest field would be C3 bonded to an
unsubstituted phenyl, C2 bonded to an unsubstituted phenyl, C3 bonded
to a substituted phenyl, and C2 bonded to a substituted phenyl.

The polymers reported in the literature (References 5 and 6)
have an OR group at the 6 position where R is aromatic. By anal-
ogy with the 2 substituted naphthalenes, the ordering of the four
C2 and C3 chemical shifts from lowest to highest field would be
C3 bonded to an unsubstituted phenyl, C3 bonded to a substituted
phenyl, C2 bonded to an unsubstituted phenyl and C2 bonded to a
substituted phenyl. This difference in ordering compared to the
halogens is due to the fact that the operative substituent effects
are positive only at C3.

Since the polymers and model compounds have been dissolved
in different solvents which show solvent effects, it is apparent
that the substituent effects vary with solvent. However, as long
as the polymer and the model compounds used to determine the sub-
stituent effects are measured in the same solvent, the results
are consistent.

Table 8 shows the substituent chemical shifts for the
model compounds and polymers considered. The small effect of the
2 or 3 substituent on the adjacent carbon has been neglected. By
combining these substituent effects, the chemical shifts of the

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TABLE 8

^{13}C SUBSTITUENT CHEMICAL SHIFTS FOR C2 AND C3 OF
2 OR 3 AND 6-SUBSTITUTED QUINOXALINE COMPOUNDS

| | | Solvent | |
2 or 3-Substituent	CdCl$_3$[11]	HCCl$_2$-CHCl$_2$[5]	DMSOd$_6$[6]
m-bromo phenyl	−1.69		
m ethynyl phenyl	−1.07		
para substituted phenyl		−.72	
para substituted phenyl			−.6
6-Substituent Effect on C2			
I	+.49		
C≡CH	+.59		
O-Ar		−.84	−.2
6-Substituent Effect on C3			
I	+.59		
C≡CH	+.89		
O-Ar		+.59	+1.2

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C2 and C3 carbons for the 2 or 3 and 6-substituted quinoxaline compounds and polymers can be assigned provided the solvent effects are considered or the same solvent is used.

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